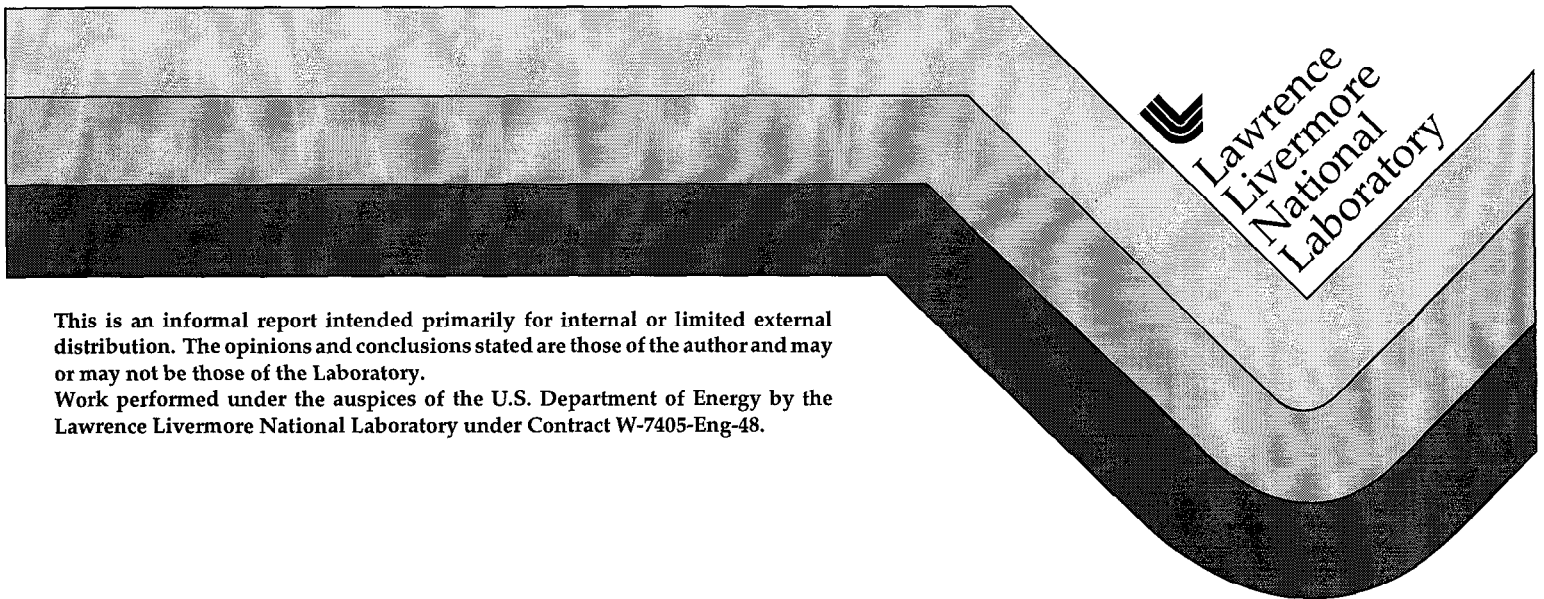# Assessing Materials ("Getters") to Immobilize or Retard the Transport of Technetium Through the Engineered Barrier System at the Potential Yucca Mountain Nuclear Waste Repository

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Abstract

Current performance assessment calculations show that technetium (Tc) and neptunium (Np) will deliver the major fraction of the radiation dose to the accessible environment from the potential Yucca Mountain nuclear waste repository. Therefore, materials that can immobilize or delay the transport of Tc or Np ("getters") are being considered for addition to either the waste-package or the backfill adjacent to the waste-package. Of the two radionuclides, Tc presents the greater challenge in identifying a suitable getter material. This report identifies several materials that warrant further consideration for immobilizing and/or sorbing Tc as additives to the backfill, and recommends active carbon and an inorganic oxide for initial testing. Other materials, such as zero valent iron, might be useful as getters if they were placed in the waste package itself, a subject that merits further investigation.

Background

Statement of the problem - Based on current source term assumptions, Total System Performance Assessment (TSPA) calculations suggest that technetium (Tc) and neptunium (Np) will deliver the major fraction of the radiation dose to the accessible environment within the first 100,000 thousands years after waste emplacement (CRWMS/M&O, 1998; pg. 11-42). Consequently, to provide a greater margin of safety for current groundwater infiltration and waste package failure scenarios, or meet safety requirements for scenarios having higher groundwater infiltration rates, or less robust waste packages, materials that can immobilize or delay the transport of Tc or Np (getters) are being considered for addition to either the waste-package or the backfill adjacent to the waste-package.

Of the two radionuclides, Tc presents the greater challenge in identifying a suitable getter material. Tc is not constrained by solubility limits under oxidizing conditions, does not interact strongly with most minerals under oxidizing conditions, and is essentially nonretarded by the rocks at Yucca Mountain. In contrast, Np is released from the spent fuel waste form at a much slower rate than Tc, is limited in concentration by incorporation into uranium-bearing secondary phases or by precipitation as an oxide/hydroxide, and is strongly sorbed/immobilized by a variety of readily available natural materials (e.g., apatite) as well as waste package corrosion products and cementitious invert materials. This report identifies several materials that warrant further consideration for immobilizing and/or sorbing Tc within the waste package or as additives to the backfill, and recommends candidate materials for initial testing.

Redox chemistry of technetium – The form of dissolved Tc, the solid phases that may limit its concentration, and its mobility in the environment are strongly influenced by redox potential (Eh) and pH (Lieser and Bauscher, 1987; 1988). Under oxidizing conditions, dissolved Tc exists primarily in the +7 valence state as the pertechnetate anion (TcO_4^-) (Kunze et al., 1996; Lieser and Bauscher, 1988; Rard, 1983) (Figure 1). For systems that are reducing (i.e., below the TcO_4^- stability field shown in Figure 1), dissolved Tc exists in the +4 valence, primarily as the $TcO(OH)_2(aq)$ species. Technetium concentrations are effectively unconstrained by solubility limits for Eh and pH in the oxidizing region because there are no sparingly soluble Tc-bearing phases that are likely to form. Because pertechnetate is anionic, it is essentially unretarded by most natural materials and is highly mobile (Gu et al., 1996; Lieser and Bauscher, 1987; 1988; Palmer and Meyer, 1981). In contrast, under reducing conditions, solubility limits, and/or sorption render Tc relatively immobile (Lieser and Bauscher, 1987; 1988).

Expected redox state of the EBS/NFE – The vadose zone at Yucca Mountain and the Engineered Barrier System/Near Field Environment (EBS/NFE) of the proposed repository are assumed to be oxidizing and expected to remain so through the pre-closure period. Expulsion of air by the production of steam during the post-closure thermal period, consumption of oxygen by interaction with introduced materials (e.g., corrosion allowance steel overpack, steel basket material, UO_2 in spent fuel), and consumption of oxygen due to microbial metabolism could potentially create periods during which the repository, or zones within it, would be reducing. However, it is currently thought that the gas phase in the near-field environment would return to ambient (i.e., oxidizing) conditions after ~4000 years in the center of the repository, and after ~1000 years at the margins (CRWMS/M&O, 1998; Table 4-8; pg. 4-80). Although a return to the ambient gas phase composition does not necessarily mean oxidizing conditions would strictly hold for all parts of the EBS/NFE, unless materials are introduced to the EBS/NFE that can be credibly predicted to maintain Eh-pH in the reducing field for the lifetime of the waste packages, a conservative assumption is that the entire EBS/NFE environment will be oxidizing when waste

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packages fail. Therefore, getter materials that can effectively retard Tc under oxidizing conditions will be required.

Bounding expected Tc concentrations – To rationally develop a set of criteria for assessing the potential of various materials to retard and/or immobilize Tc, and to develop realistic design criteria, it is critical to bound the expected concentration of Tc leaving the waste packages. Both the type of getter material and the mass required for its effectiveness will be strongly influenced by the range in Tc concentrations expected from the waste-package. Current TSPA calculations assume an 8-order of magnitude concentration range for Tc leaving the waste package (3.6×10^{-7} - 10 M) (CRWMS/M&O, 1998; Table 6-32). The assumed concentrations are several to many orders of magnitude larger than dissolved Tc concentrations measured in laboratory spent fuel leaching tests.

Experimental spent fuel leach tests have confirmed that Tc is released at a greater rate than uranium and Np, from oxidative dissolution of metallic Tc-bearing particles (ϵ-phase) or from UO_2 grain boundaries (Stout and Leider, 1998; pg. 2.1.3.5-35). Even though Tc is released at a greater rate than the actinide components of the waste form, and under the Eh-pH conditions of the tests its concentration should not be constrained by solubility limits, the observed concentrations of Tc are apparently limited by the overall spent fuel dissolution rate. For example, under oxidizing conditions, the concentration of Tc released from spent fuel is on the order of 10^{-8} – 10^{-7} M for fully saturated static leach tests (e.g.; (Wilson, 1990); Tables A.2-A.5) and unsaturated drip tests (Stout and Leider, 1998; Table 3.4.2-7; pg. 3.4.2-42). The observed dissolved Tc concentrations in the saturated tests are, in fact, similar to solubility-limited Tc concentrations predicted for redox conditions in the $TcO(OH)_2(aq)$ stability field using existing thermodynamic data (see Figure 1). The predicted Tc concentration for these Eh/pH conditions, $\sim 3 \times 10^{-8}$ M based on the solubility of $TcO_2 \cdot 2H_2O(am)$ (based on GEMBOCHS thermodynamic database thermo.com.V8.R6.230 (Johnson and Lundeen, 1994)), is <u>five</u> orders of magnitude lower than the average Tc concentration (10^{-3} M) assumed in TSPA-VA calculations (CRWMS/M&O, 1998; Table 6-32). The choice of Tc concentrations used for PA calculations is significant. For example, when the 'equilibrium' film concentration of radionuclides deduced from spent fuel drip tests (Stout and Leider, 1998; Table 3.4.2-7; pg. 3.4.2-42) are used for performance assessment calculations, the dose to the accessible environment at 100,000 years is decreased by ~25-fold compared to base case calculations (CRWMS/M&O, 1998; Figure 6-60; pg. 6-142).

Because the far-field environment does not provide a sorptive barrier to Tc transport, even the low concentrations of Tc observed in spent fuel leach tests could pose a performance problem. Furthermore, although the experimentally observed Tc releases from spent fuel are orders of magnitude lower than TSPA assumptions, a scenario can be envisioned (e.g., alternating periods of unsaturated and saturated corrosion of spent fuel under oxidizing conditions) which could lead to much higher dissolved Tc concentrations (Stout and Leider, 1998; pg. 2.1.3.5-34).

The physical and chemical properties and mass of a potential getter required to yield a specified level of performance will be directly related to the concentration of Tc expected in the groundwater exiting the waste package. Clearly, a more realistic assessment of the expected range and average concentration of Tc is necessary. Until a more reasonable range of expected Tc concentrations exiting the waste package is utilized for performance assessment, the search for materials that could significantly retard Tc transport could be hampered by overly stringent requirements for immobilization capacity, and hence potentially useful materials could be ruled out.

Potential materials for Tc retardation/immobilization

Selection criteria - Although specific properties required for a Tc getter material cannot be completely defined at this stage, potential getter materials can be assessed using criteria listed below.

1. *Retardation/immobilization properties* – a) The getter material must display at least a moderate ability to adsorb/immobilize Tc from chemically simple solutions. b) The mass/volume of getter material required to provide the specified reduction in Tc-derived dose at the accessible environment is reasonable for emplacement in backfill or within waste packages (i.e., the sorptive/immobilization capacity is sufficiently large). c) The material will adsorb/immobilize Tc from the chemically complex radionuclide-bearing groundwater that has contacted the waste form, and will exhibit the required activity across the chemical regime (Eh, pH, ionic strength, composition) that is expected in the EBS/NFE. d) The sorption/immobilization of Tc can be reasonably predicted using a combination of laboratory bench scale experiments and geochemical models.
2. *Longevity* – a) The getter material must be able to survive the post-closure environment and retain the required sorptive/immobilization activity. b) The expected long-term behavior of the material can be credibly defended using a combination of experiment, natural occurrence, and field studies.
3. The getter material will not adversely affect water chemistry or other EBS/NFE components from the perspective of repository performance, nor contribute additional toxic substances to the source term.
4. The getter material can be formulated to be compatible with hydrologic requirements of backfill/invert/filler.
5. Getter material emplacement is technically feasible.
6. Getter material expense is not prohibitive.

A successful getter material should substantially meet all six of the above criteria. The following sections list materials that have been observed to have sorptive/immobilization properties for Tc – i.e., they meet criterion (1a). Those that by inspection could potentially meet the remaining parts of criterion (1) and criteria (2), (3), and (4) are discussed more fully, and are proposed to be examined in more detail via experiment and modeling. Criteria 5 and 6 were not used for selecting or rejecting any of the materials considered.

Minerals under oxidizing conditions– With the exception of certain sulfide and reduced valence metal oxide minerals, retardation of Tc by natural materials under oxidizing conditions is very limited; most partition coefficients (K_d's), are less than 10 mL/g (Ito and Kanno, 1988; Table 1; Lieser and Bauscher, 1987; pg. 213; 1988; pg. 125; Strickert et al., 1980; pg. 253). The partitioning of Tc to the solid phase via sorption under oxidizing conditions is thought to occur primarily by anion exchange (Palmer and Meyer, 1981; pg. 2980). Natural materials that have significant anion exchange capacities, such as imogolite, hydrotalcite, and oxides of aluminum, zirconium, and iron have been shown to display small to moderate K_d's for Tc, and could possibly provide limited to moderate retardation capability (Balsley et al., 1998; Palmer and Meyer, 1981).

For some minerals, such as reduced valence metal sulfides and arsenides (stibnite (Sb_2S_3); galena (PbS); bournonite ($CuPbSbS_3$); chalcocite (Cu_2S); covellite (CuS); chalcopyrite ($FeCuS_2$); pyrrhotite (FeS); löllingite ($FeAs_2$); enargite (Cu_3AsS_4)), partitioning of Tc to the solid phase can

be quite significant (Bock et al., 1989; Strickert et al., 1980; Zhuang et al., 1988). These observations are explained not by ion exchange, but by reduction of Tc(VII) to Tc(IV) and precipitation as $Tc(OH)_4$ or TcO_2, or as precipitation of technetium sulfide (Bock et al., 1989; pg. 976; Lieser and Bauscher, 1988; pg. 127). Reduced valence metal oxides, carbonates, and silicates have also been shown to display moderate K_d's for Tc (tenorite (CuO); cuprite (Cu_2O); siderite ($FeCO_3$); azurite ($Cu_3(CO_3)_2(OH)_2$; crysocolla ($CuSiO_3$)·$2H_2O$)) (Balsley et al., 1998; Strickert et al., 1980; Zhuang et al., 1988). Although partition coefficients for these reduced metal phases were obtained from experiments carried out under nominally oxidizing conditions, in the absence of observed precipitation of sulfides, immobilization of Tc by reduction of Tc(VII) to Tc(IV) is presumed to have occurred at the mineral surface.

Minerals under reducing conditions – Under reducing conditions the +4 valence is the most stable form of dissolved Tc (Figure 1). When dissolved Tc is predominantly Tc(IV), the formation of relatively insoluble $Tc(OH)_4$ or TcO_2 will control dissolved Tc concentrations at $\leq~10^{-8}$ M. However, because the rate of reduction of Tc in solution from the +7 to +4 state is kinetically inhibited (Cui and Eriksen, 1996; pg. 2267), lowering the redox state of the system may not necessarily result in an increase in partitioning to the solid phases. Reduction of TcO_4^- is promoted by dissolved Fe(II), but mineral surfaces, and specifically Fe(II)-bearing mineral surfaces, are also apparently necessary for the rate of reduction to be significant (Byegard et al., 1992; pg. 242; Cui and Eriksen, 1996; pg. 2267). Thus, in order for reductive immobilization to occur, the system must be reducing, Fe(II) or other easily oxidized species must be present, and surface sites at which reduction can take place must be available.

As an example of the strong effect of redox on partitioning, at pH 7 the K_d for Tc on iron-bearing sediment samples increases by almost four orders of magnitude as Eh decreases from about +300 to +100 mV (Figure 2). At pH 4, the increase in K_d occurs between +400 and +200 mV (Lieser and Bauscher, 1988). As the pH increases, the Eh required for Tc reduction decreases, hence estimates of redox for the EBS or within the waste package will be quite important. The types of Fe(II)-bearing minerals that have been implicated in reductive sorption/immobilization of Tc include biotite, magnetite, chlorite, olivine, hornblende, and clay minerals.

Other materials – Besides common minerals and rocks, other materials have been utilized or proposed for retardation and/or immobilization of Tc (as TcO_4^-) from process streams and/or groundwaters. These include, anion exchange resins (Delcul et al., 1993), zero valent iron (Fe(0)) (Delcul et al., 1993; Kunze et al., 1996; Liang et al., 1996; Strickert et al., 1980), activated carbon (Gu et al., 1996; Ito and Akiba, 1991; Ito and Kanno, 1988; Ito and Yachidate, 1992; Yamagishi and Kubota, 1989; Yamagishi and Kubota, 1993), lignite and coal (Balsley et al., 1998), organic phosphates (Akopov et al., 1990; Elkolaly et al., 1990), bone char (Krumhansl, 1998), calcium mono sulfate aluminate (Balsley et al., 1998), and organic liquids (Chaiko et al., 1995). These materials, especially activated carbon and zero valent iron, are much more effective sorbents under oxidizing conditions than any of the non-sulfide natural materials mentioned above.

Microbial immobilization – Under anaerobic conditions certain bacteria are capable of reducing Tc and immobilizing it (Lloyd et al., 1997; Lloyd et al., 1998; Macaskie et al., 1996). Formation of Tc(IV) oxides and/or Tc(VII) sulfides have been proposed as the Tc-bearing phases that precipitate during bacterial metabolism to reduce the dissolved Tc concentration.

Based on parts of criteria (1), (2), (3), and (4), some of the potential materials described above can easily be rejected from further consideration (Table 1). Getter materials not rejected are

listed in Table 2.. Several of the materials not rejected, such as Fe(II)-bearing minerals or zero valent iron, may not meet criterion (2a) unless placed within the waste package, an alkaline cementitious material, or it can be shown that the EBS/NFE chemical environment is now, and will remain, conducive to their longevity and activity. These phases are included for consideration because design options have not been finalized, and the expected evolution of the repository chemical environment is still not well known.

Inorganic oxides and hydroxides -- Corundum (Al_2O_3), boehmite (AlOOH), goethite (FeOOH), and ZrO_2 show moderate sorptive properties for Tc (Table 2) that are pH and ionic strength dependent (Krumhansl, 1998; Palmer and Meyer, 1981). For experiments in which pH and ionic strength were varied, K_d's were found to vary inversely with pH and ionic strength, suggesting that sorption was due to anion exchange and/or surface complexation. Because of the very low solubility of these phases under the range of chemical conditions expected in the repository, and their occurrence in oxidized soils and sediments, the longevity of these materials could be credibly assured. However, the hydrous phases, boehmite and goethite, could potentially be dehydrated during the thermal pulse, and hence altered to Al_2O_3 or Fe_2O_3, which could negatively impact activity. Because sorption is limited to the surfaces of these phases, the specific surface area of the material would need to be large. Hence, long-term dissolution/reprecipitation processes that might reduce surface area would reduce the sorptive capacity of the getter. Although these K_d's are low to moderate, their longevity, common availability, lack of obvious deleterious effects on other EBS components, and potential for emplacement in a variety of forms (powders, aggregates, coatings; etc) makes them suited for further consideration.

Active carbons -- Active carbons are formed by pyrolysis of organic matter, resulting in a high specific surface material with organic functional groups that are capable of adsorbing a wide variety of organic and inorganic species (Boehm, 1994; Wigmans, 1989). The specific properties of active carbons depend on the source of the organic material used to create the carbon, and method used to pyrolyze and activate the product. Under nominally oxidizing conditions the K_d's for Tc on active carbons are very high ranging from 10^2 mL/g in chemically complex extremely high ionic strength reprocessing raffinates (Yamagishi and Kubota, 1993; pg. 717), to >10^4 mL/g in groundwater (Gu et al., 1996; pg. 131). Sorption of Tc is pH and ionic strength dependent, and Tc can be completely desorbed by treatment with high concentrations of certain anions. These observations have been used to postulate that sorption occurs via anion exchange. The type of active carbon also affects the K_d observed. For example, Ito and Yachidate (1992; Figure 1) observed K_d's varying from 10^1 to 10^4 mL/g depending on active carbon type for Tc adsorption from 1 M chloride and nitrate solutions at varying pHs. The observation that pertechnetate can be sorbed by active carbons from solutions having 10^8 greater concentrations of other anions suggests that surface complexation or specific adsorption is involved in addition to anion exchange (Gu et al., 1996; pg. 126).

The expected longevity of active carbons in the EBS/NFE could be assessed and bounded by comparison with the longevity of charcoals (natural active carbons). Radiocarbon dating has shown that some charcoals have survived in soils and sediments in excess of $3-5x\ 10^4$ years. These charcoals have clearly survived exposure to long-term microbial and chemical processes for thousands of years in a variety of environments. Charcoals are also used to date volcanic debris and ash flows; hence, they resist thermal oxidation.

The longevity of charcoals not only provides a means for assessing the longevity of active carbons, but age-dated charcoals could also be used to assess whether the sorptive properties of carbon change significantly with age. In addition, hydrothermal treatment of active carbons at elevated temperatures and relative humidities can provide an accelerated assessment of the changes in sorptive properties to be expected in a carbon barrier exposed to near-field conditions.

The systematic effects of pH, ionic strength, and surface functional group variation on adsorption by activated carbons suggest that sorption could be modeled using a surface complexation approach similar to that used for oxide surfaces. Laboratory experiments and analysis of field derived charcoals could be integrated to obtain a credible assessment of the evolution of activity of carbon over repository relevant time periods.

Zero valent iron -- Zero valent iron has been also been shown to effectively remove Tc from groundwater (Liang et al., 1996; pg. 121). K_d's for Tc adsorption as high as 1.6×10^3 mL/g have been observed in a nominally oxidizing groundwater. Active oxidation of Fe(0) to Fe(II) at the surface of the iron is required to reduce Tc(VII) to Tc(IV) and subsequent immobilization as a relatively insoluble oxide. In contrast to active carbon, the immobilization of Tc by zero valent iron is not readily reversible, that is; the kinetics of dissolution of the precipitated Tc oxide will control remobilization of Tc, rather than simple desorption.

Because active oxidization of zero valent iron is required for immobilization, iron that is emplaced outside the waste package would be expected to be completely oxidized by the time waste packages fail, and thus have lost its ability to immobilize Tc. However, zero valent iron placed inside a waste package could retain its activity until the package is breached and the waste form begins dissolving. (Kunze et al., 1996) showed that zero valent iron was very effective in reducing Tc concentrations under simulated near-field conditions. An example of how effective iron could be is shown by the observation that Tc concentrations dropped to below detection limits in a spent fuel leach test in which unanticipated corrosion of a stainless steel container occurred during the test (Stout and Leider, 1998; pg. 2.1.3.5-8).

Imogolite – Imogolite is a thread-like tubular aluminosilicate mineral found primarily in young soils formed from volcanic ash. The mineral generally has a high specific surface and can have a significant anion exchange capacity at pHs below 6 (e.g., ~3.0 meq/g) (Wada, 1989; pgs. 1062,1070). The anion exchange capacity is strongly pH dependent, and at pHs above 8 would be expected to be very small. Because imogolite is only found in young sediments or soils, its longevity in the repository would be questionable.

Calcium mono sulfate aluminate (CMSA) – This compound exhibits a moderate K_d for Tc (Balsley et al., 1998; Table 3), but because it is formed in alkaline environments such as concretes, would not be expected to survive unless it was incorporated into a concrete or other cementitious barrier.

Hydrotalcite – Hydrotalcites are layered minerals possessing a significant anion exchange capacity (Balsley et al., 1998; Table 3). The stoichiometry of these phases is quite variable, and can range from magnesium aluminum hydroxy carbonate to zinc aluminum hydroxy chloride. A common feature of these compounds is that they are either found or synthesized under high pH conditions. Hence, their stability outside of a cementitious barrier would not be expected in the long term.

Fe(II)-bearing minerals – There are many minerals that contain a significant amount of Fe in the divalent state. Their ability to sorb Tc is only realized under reducing conditions (Figure 2), hence their utility as a barrier to Tc movement would be limited in an oxidizing repository. Emplacement of these materials could be considered within the waste package if the redox state in the package could reasonably be expected to be reducing during waste form dissolution.

Material recommended for further testing

Based on potential Tc getters recommended for further consideration (Table 2), two materials are recommended for the first round of testing: active carbon and one of the inorganic oxides. Because the focus of this report is on materials that could be added to the drift (i.e., outside the waste package), zero valent iron is not recommended for further testing at this point. However, assessing the benefits of having many tons of steel waste package internals corroding simultaneously with waste form dissolution, clearly merits further investigation.

A plan for testing active carbon and an iron oxide to assess their suitability as Tc getters is currently being prepared. This testing will include three main activities:

(1) Batch studies to assess sorptive activities and derive sorption model parameters as a function of pH, dissolved carbonate, and the concentration of other waste-form derived species.

(2) Thermal treatments to assess stability and activity of getters under repository conditions

(3) Column experiments for a limited set of chemical conditions to assess particle size, porosity, and packing effects on transport, and to help validate transport models

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Table 1.   Potential Tc getter materials rejected from further consideration.

Rejected Material	Criteria failed*/Remarks
Sulfides, arsenides	(2,3) – unstable in the long term in an oxidizing environment; potential for lowered pH due to generation of H_2SO_4 during oxidation.
Reduced transition metal oxides, carbonates, and silicates	(2,3) – oxidation to higher valences and loss of activity likely in an oxidizing environment; potential for increase in toxic metals in source term.
Organic liquids	(2,4) – probably impossible to assure long term stability and activity; emplacement will be difficult.
Lignite and coal	(3) – sulfide impurities will likely oxidize and lower pH due to H_2SO_4 production.
Organic phosphates	(2) – probably impossible to assure long term stability and activity.
Anion exchange resins	(2) – probably impossible to assure long term stability and activity.
Microbial immobilization	(2) – probably impossible to assure that required nutrient source and redox state will exist at the time waste packages fail.

*2= Longevity of getter in repository environment, 3 = adverse affect on other areas of repository performance, 4 =incompatibility issues. See text for further discussion.

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Table 2.   Potential Tc getter materials for further assessment

Material	K_d mL/g	Form	Remarks	References
Corundum (Al_2O_3)	10^0-10^2	Fine particles or aggregates of fine particles	Significant pH and ionic strength dependence	(Palmer and Meyer, 1981; Fig. 4 & 6)
Boehmite (AlOOH)	10^1-10^2	Fine particles or aggregates of fine particles		(Krumhansl, 1998)
ZrO_2	10^0-10^2	Fine particles or aggregates of fine particles	Significant pH and ionic strength dependence	(Palmer and Meyer, 1981; Fig. 3 & 5)
Goethite (FeOOH)	10^1	Fine particles or aggregates of fine particles		(Krumhansl, 1998)
Imogolite (alumino-silicate)	10^1	Fine particles	Longevity must be assessed	(Balsley et al., 1998; Table 3)
CMSA (calcium mono sulfate aluminate)	10^2	Within cementitious materials	Longevity outside of concrete is questionable	(Balsley et al., 1998; Table 3)
Fe(II)-bearing minerals	10^3	Fine particles or aggregates of fine particles	Eh/pH must be below the TcO_4^- stability field; longevity outside of waste-package must be assessed	(Lieser and Bauscher, 1988; Figure 2)
Zero valent iron (Fe(0))	10^3	Filings or beads	Longevity outside of waste-package is questionable	(Liang et al., 1996; pg. 121)
Active carbons	10^2-10^4	Millimeter to cm scale particles	pH and ionic strength dependence	(Gu et al., 1996; pg. 131; Ito and Yachidate, 1992; Fig. 1)
Hydrotalcite (variable)	10^2	Within cementitious materials	Longevity outside of concrete is questionable	(Balsley et al., 1998; Table 3)

Figure showing Eh-pH (Pourbaix) diagram for Tc at 25 °C. Axes: Eh (volts) from -.6 to .8 on the vertical axis, pH from 0 to 10+ on the horizontal axis. Labeled stability fields include TcO^{++}, TcOOH$^+$, Tc^{+++}, TcO(OH)$_2$(aq), and TcO$_4^-$. Annotation: "Eh/pH path for calculating solubility of TcO$_2$·2H$_2$O(am)".
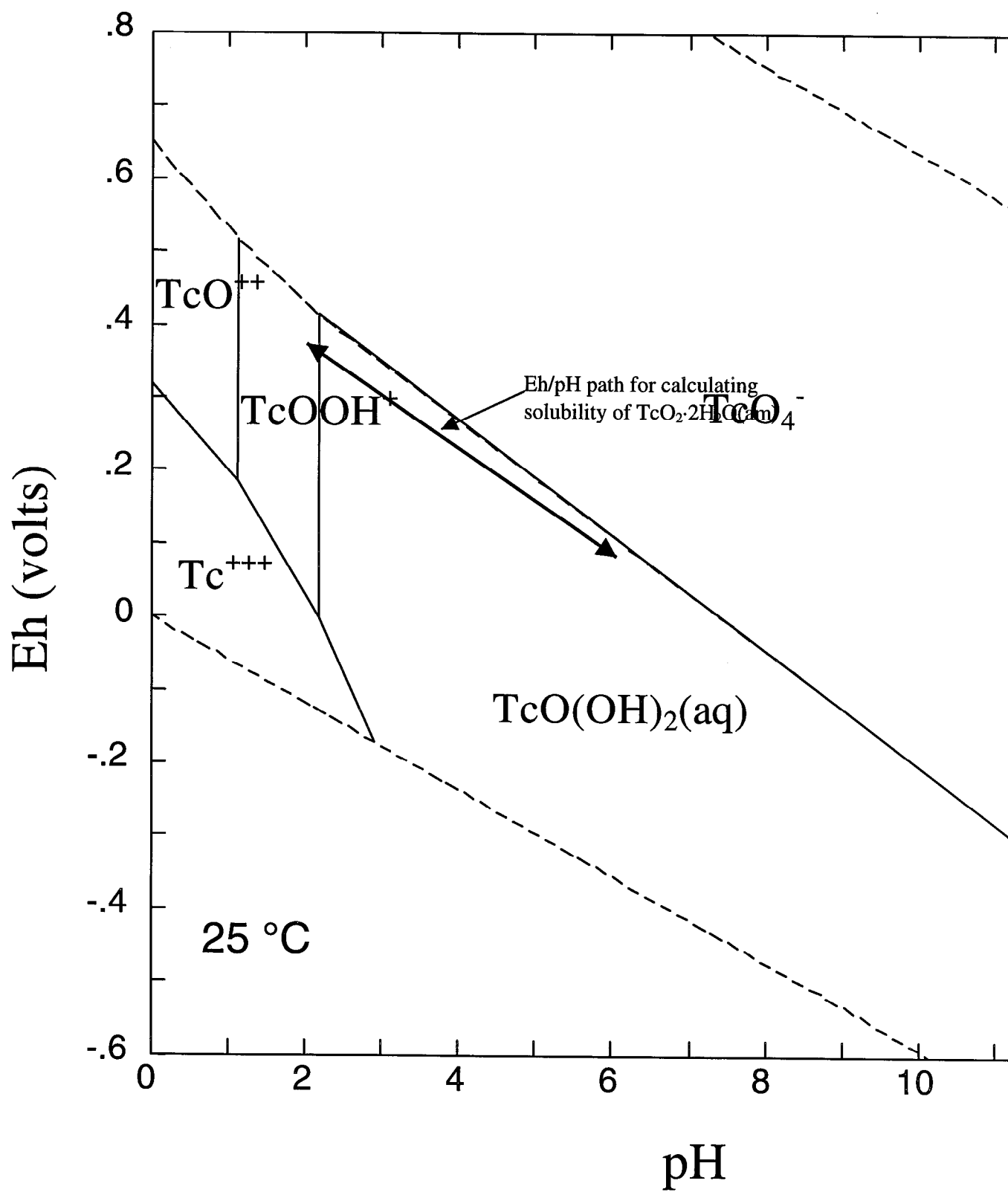
Figure 1. Activity diagram showing predominant dissolved Tc species over Eh-pH space. (Data from GEMBOCHS database thermo.com.V8.R6.230; T=25 °C, Tc=10^{-10} M, fugacity CO_2=$10^{-3.52}$ (Johnson and Lundeen, 1994)).
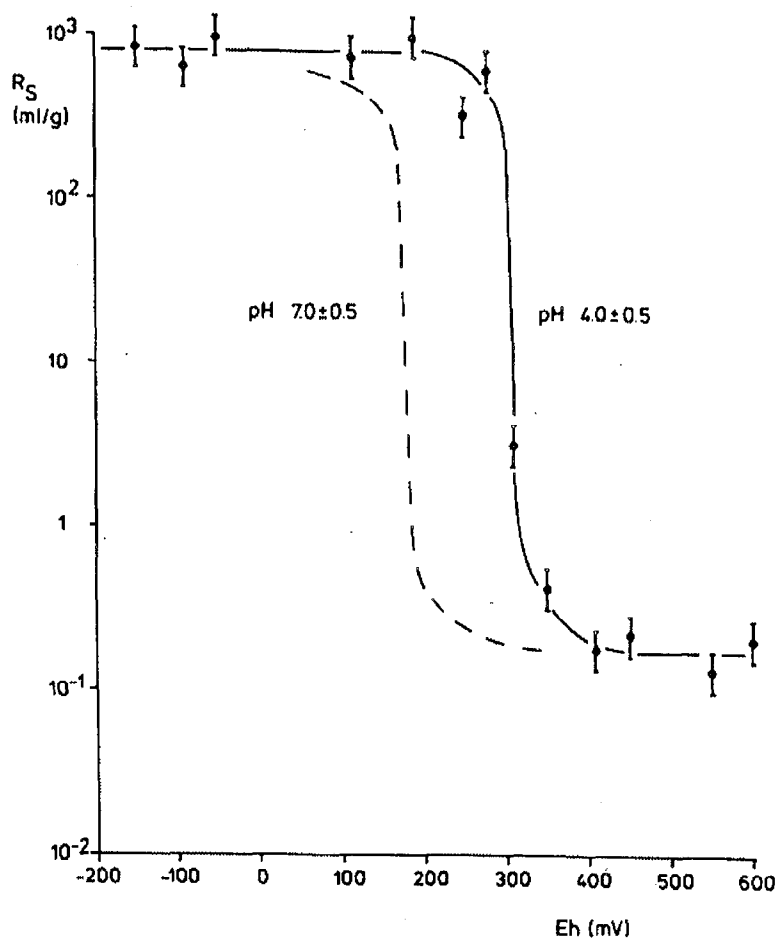

Fig. 2. Sorption ratio R_S as function of the redox potential Eh at pH 4.0 ± 0.5 (for comparison: curve obtained at pH 7.0 ± 0.5 [1])

Figure 2. Scanned image of Figure 2 from Lieser and Bauscher (1988) showing K_d (R_s) vs. Eh for iron-bearing sediments at pH 4 and 7.

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